LIQUID AND SOLID PHASE MICROEXTRACTION METHODS FOR THE ANALYSIS OF ORGANIC ENVIRONMENTAL POLLUTANTS

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ABSTRACT

This work involves the investigation of new approaches and applications in miniaturized sample preparation techniques based on liquid phase and solid phase microextractions. A two-phase hollow fiber liquid phase microextraction (HF-LPME) method combined with gas chromatography-mass spectrometry was developed for the determination of selected polycyclic aromatic hydrocarbons (PAHs) in fresh milk. Under optimized conditions, low detection limits (LODs) were obtained ranging from 0.07-1.4 μg L^{-1} with relative recoveries of 85-110% which were higher than those obtained by conventional solvent extraction for the volatile PAHs. Agarose film liquid phase microextraction (AF-LPME) was developed for the extraction and preconcentration of PAHs in environmental water samples. Agarose, a green polymer, has been manipulated for different microextraction approaches. Agarose film was used as an interface between donor and acceptor phases which allowed for selective extraction of the analytes under optimum conditions. Under the optimum extraction conditions, the method showed good linearity in the range of 0.1–200 μg L^{-1}, low limits of detection (0.01-0.04 μg L^{-1}) and satisfactory relative recoveries (92.9-104.7%). AF-LPME device proved to be low-cost and thus reuse or recycle of the film was not required to eliminate the analytes carry-over between runs. A new microextraction technique termed agarose gel liquid phase microextraction (AG-LPME) was developed for the extraction of PAHs in water. Solvent-impregnated agarose gel disc used in AG-LPME was prepared by slicing gelled agarose and exchanging the solvent from water to ethanol and then to 1-octanol that functioned as the extractant and impregnation solvent. The solvent impregnated AG-LPME was found to be comparable with HF-LPME in terms of extraction efficiencies without solvent dissolution problems observed. The method offered high enrichment factors in the range of 89-177 and trace level LODs in the range of 9-14 ng L^{-1}. This technique combines extraction and preconcentration approaches using an environmentally-compatible solvent holder that fulfils the green chemistry concept. Due to the hydrophilic property of agarose, the selectivity of AG-LPME was evaluated on hydrophilic triazine herbicides. The AG-LPME showed significantly higher extraction efficiencies as compared to HF-LPME. The method offered superior enrichment factors in the range of 115-300 and trace LODs in the range of 0.02-0.04 μg L^{-1}. Multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT-AFME) combined with micro high performance liquid chromatography–ultraviolet detection has also been developed. The method utilized MWCNTs immobilized in agarose film which served as the adsorbent holder. The technique achieved trace LODs in the range of 0.1-50 ng L^{-1} for selected PAHs. The new MWCNT-AFME method was successfully applied to the analysis of spiked green tea beverage samples with good relative recoveries. The results supported the feasibility of agarose to serve as adsorbent holder in solid phase microextraction, thus saving the cost of chemical and waste disposal.

ABSTRAK

Kerja ini melibatkan kajian pendekatan dan aplikasi baru dalam teknik mini penyediaan sampel berdasarkan pengekstrakan mikro fasa cecair dan pepejal. Kaedah pengekstrakan mikro fasa cecair membran gentian berongga (HF-LPME) jenis dua fasa digabung dengan kromatografi gas-spektrometri jisim dibangunkan untuk menentukan hidrokarbon aromatik polisiklik (PAHs) dalam susu segar. Pada keadaan optimum, had pengesanan (LOD) rendah (0.07-1.4 μg L^{-1}) diperoleh dengan perolehan balik relatif 85-110% yang lebih tinggi daripada pengekstrakan pelarut konvensional untuk PAHs meruap. Pengekstrakan mikro fasa cecair filem agarosa (AF-LPME) dibangunkan untuk mengekstrak dan pra-memekatkan PAHs dalam air persekitaran. Agarosa, sejenis polimer hijau, telah dimanipulasikan untuk pendekatan pengekstrakan mikro berlainan. Filem agarosa digunakan sebagai antaramuka di antara fasa penderma dan penerima untuk membolehkan pengekstrakan selektif analit pada keadaan optimum. Pada keadaan pengekstrakan optimum, kaedah ini menunjukkan kelinearan baik dalam julat 0.1-200 μg L^{-1}, LOD rendah (0.01-0.04 μg L^{-1}) dan perolehan balik relatif memuaskan (92.9-104.7%). Oleh kerana peralatan AF-LPME berkos rendah, penggunaan semula atau pengitaran semula filem agarosa tidak diperlukan bagi menghindari pencemaran analit antara larian. Satu teknik pengekstrakan mikro baru dinamakan pengekstrakan mikro fasa cecair gel agarosa (AG-LPME) dibangunkan bagi menentukan PAHs dalam air. Cakera gel agarosa terkandung pelarut yang diguna dalam AG-LPME disediakan dengan memotong agarosa yang telah membentuk gel dan menukar pelarut daripada air kepada 1-oktanol yang berfungsi sebagai pelarut pengekstrak dan impregnasi. Kaedah ini didapati setanding dengan HF-LPME dari segi keberkesanan pengekstrakan tanpa masalah kehilangan pelarut. Kaedah ini menawarkan faktor pengkayaan yang tinggi (89-177) dan LOD aras surih dalam julat 9-14 ng L^{-1}. Teknik ini menggabungkan pengekstrakan dan pra-pemekatan menggunakan pemegang pelarut yang serasi dengan persekitaran dan bersesuaian konsep kimia hijau. Disebabkan sifat agarosa yang hidrofilik, kepilihan AG-LPME seterusnya dinilai menggunakan racun rumpai triazina hidrofilik. AG-LPME menunjukkan keberkesanan pengekstrakan yang ketara lebih tinggi berbandingkan HF-LPME. Kaedah ini menawarkan faktor pengkayaan unggul (115-300) dan LOD aras surih dalam julat 0.02-0.04 μg L^{-1}. Pengekstrakan mikro karbon tiub-nano berbilang dinding yang terkandung dalam filem agarosa (MWCNT-AFME) digabung dengan kromatografi cecair prestasi tinggi mikro-pengesanan ultra lembayung telah dibangunkan. Kaedah ini menggunakan karbon tiub-nano berbilang dinding yang tidak bergerak dalam filem agarosa untuk berfungsi sebagai pemegang bahan penjerap. Teknik ini mencapai LOD aras surih dalam julat 0.1-50 ng L^{-1} bagi PAHs terpilih. Kaedah MWCNT-AFME baru ini telah berjaya diaplikasi dalam analisis minuman teh hijau yang dipakukan dengan perolehan semula relatif yang baik. Keputusan kajian ini menyokong kebolehan agarosa untuk berfungsi sebagai pemegang bahan penjerap pengekstrakan mikro fasa pepejal dan menjimatkan kos bahan kimia dan pelupusan sisa.